

AD-A235 903

(2)

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE



## REPORT DOCUMENTATION PAGE

DD FORM 173, JUN 86  
DAF No. 701 0188

1a. REPORT SECURITY CLASSIFICATION Unclassified			1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT for unlimited distribution and release	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			MAY 23 1991	
4. PERFORMING ORGANIZATION REPORT NUMBER(S) 1148-01			5. MONITORING ORGANIZATION REPORT NUMBER	
6a. NAME OF PERFORMING ORGANIZATION University of Lowell		6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research-Chemistry Division	
6c. ADDRESS (City, State, and ZIP Code) Department of Chemistry-One University Avenue Lowell, Massachusetts 01854			7b. ADDRESS (City, State, and ZIP Code) Department of the Navy Arlington, Virginia 22217-5000	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-90-J-1148	
8c. ADDRESS (City, State, and ZIP Code)			10. SOURCE OF FUNDING NUMBERS	
			PROGRAM ELEMENT NO.	PROJECT NO.
			TASK NO.	WORK UNIT ACCESSION NO.
11. TITLE (Include Security Classification) Optical and Electro-optical Properties of a Photocross-linkable Polymer				
12. PERSONAL AUTHOR(S) A.K.M. Rahman, B.K. Mandal, X.F. Zhu, J. Kumar and S.K. Tripathy				
13a. TYPE OF REPORT Technical		13b. TIME COVERED From 900601 To 910531		14. DATE OF REPORT (Year, Month, Day) 910503
15. PAGE COUNT six (6)				
16. SUPPLEMENTARY NOTATION				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)	
FIELD	GROUP	SUB-GROUP		
19. ABSTRACT (Continue on reverse if necessary and identify by block number) Planar waveguides from a photocross-linkable polymer have been fabricated on glass and SiO <sub>2</sub> on silicon using the spin coating process. The polymer has been cross-linked by exposure to UV radiation ( $\lambda = 254$ nm). Prism coupling technique has been used to couple a laser beam into the waveguide structure. The waveguiding parameters such as number of modes, loss, thickness and index of refraction of the polymer have been determined before and after cross-linking. The refractive index of the polymer before cross-linking differs significantly from that after cross-linking. No anisotropy has been observed in the refractive indices for the uncross-linked or cross-linked samples. The refractive index and thickness of the polymer film before and after cross-linking have also been measured using an ellipsometer and found to be in very good agreement with those obtained by the prism coupling technique. Dye molecules with large second order hyperpolarizability were utilized as guests into the photocross-linkable polymer matrix for second order nonlinear optical applications. Electro-optic properties of this polymeric system are reported.				
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT a) UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT. <input type="checkbox"/> DTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION Unclassified	
22a. NAME OF RESPONSIBLE INDIVIDUAL			22b. TELEPHONE (Include Area Code)	22c. OFFICE SYMBOL

DD Form 1473, JUN 86

Previous editions are obsolete

SECURITY CLASSIFICATION OF THIS PAGE

UNCLASSIFIED

91-00345



91 5 22 102

**OFFICE OF NAVAL RESEARCH**

GRANT N00014-90-J-1148

R&T Code 4132016

Technical Report No. 1



Accession For	
ALL GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	

**Optical and Electro-optical Properties of a  
Photocross-linkable Polymer**

by

**A.K.M. Rahman, B.K. Mandal, X.F. Zhu,  
J. Kumar and S.K. Tripathy**

**in Optical and Electrical Properties of Polymers**

**J.A. Emerson, and J.M. Torkelson, eds.  
MRS 214 (1991)**

**University of Lowell  
Department of Chemistry  
Lowell, Massachusetts**

**May 3, 1991**

Reproduction in whole or in part is permitted for any purpose of the United States Government

This document has been approved for public release and sale; its distribution is unlimited.

# OPTICAL AND ELECTRO-OPTICAL PROPERTIES OF A PHOTOCROSS-LINKABLE POLYMER.

A. K. M. Rahman, B. K. Mandal\*, X. F. Zhu, J. Kumar, and S. K. Tripathy\*

University of Lowell, Departments of Physics and Chemistry, Lowell, MA 01854, U.S.A.

## ABSTRACT

Planar waveguides from a photocross-linkable polymer have been fabricated on glass and  $\text{SiO}_2$  on silicon using the spin coating process. The polymer has been cross-linked by exposure to UV radiation ( $\lambda = 254\text{nm}$ ). Prism coupling technique has been used to couple a laser beam into the waveguide structure. The waveguiding parameters such as number of modes, loss, thickness, and index of refraction of the polymer have been determined before and after crosslinking. The refractive index of the polymer before cross-linking differs significantly from that after cross-linking. No anisotropy has been observed in the refractive indices for the uncross-linked or cross-linked samples. The refractive index and thickness of the polymer film before and after cross-linking have also been measured using an ellipsometer and found to be in very good agreement with those obtained by the prism coupling technique. Dye molecules with large second order hyperpolarizability were utilized as guests into the photocross-linkable polymer matrix for second order nonlinear optical applications. Electro-optic properties of this polymeric system are reported.

## INTRODUCTION

Organic nonlinear optical (NLO) polymers are potential candidates for second order nonlinear optical and electro-optic devices [1-2]. These NLO polymers provide a number of advantages over inorganic NLO materials including lower dielectric constant and greater processing flexibility. Extensive studies have been made on two types of poled NLO polymers such as guest-host systems and side chain polymers [3-7]. The side chain polymers are significantly more stable than the guest-host systems, but they still suffer from slow relaxation of nonlinearity over a period of time.

The stability of the poling induced nonlinearity is very critical to device application. Recently, Eich et al. [7] have developed a cross-linked epoxy system in which this relaxation problem has been overcome by thermal cross-linking of NLO polymers in the poled orientation. However, in order to achieve an efficient epoxy system, one needs to control the molecular weight of the epoxy prepolymer. Furthermore, very long curing and poling cycles (~20 h) at high temperature (~140°C) are necessary. More recently, a different approach to obtain a stable cross-linked polymer system by photochemical reaction has been reported by Mandal et al. [9-10]. In this technique NLO molecules and photosensitive polymer are processed in the same way as the guest-host systems and photocross-linking is then performed by exposing to UV radiation subsequent to poling.

In this paper we have presented waveguiding properties of a photosensitive polymer, polyvinyl cinnamate (PVCN) before and after photocross-linking. NLO molecules of a new azo dye 3-cinnamoyloxy-4-[4(N,N-diethylamino)-2-cinnamoyloxy phenyl azo] nitrobenzene (CNNB-R) were introduced into the PVCN matrix. Electro-optic coefficients of poled and cross-linked PVCN containing CNNB-R have been determined.

A.K.M. RAHMAN

1st page start Title here

1st page start Authors here

1st page begin Abstract here

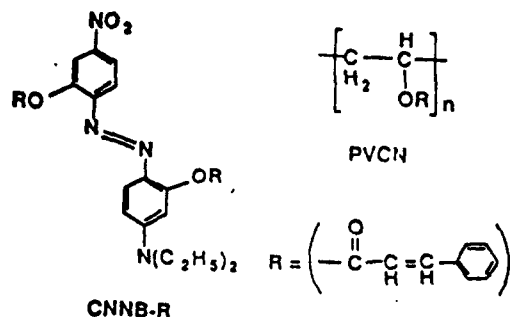


Figure 1. Structures of new azo dye CNNB-R (guest) and PVCN (host)

## THIN FILM PREPARATION

The structural formulae of PVCN and azo dye CNNB-R are shown in Figure 1. PVCN and PVCN doped with CNNB-R were dissolved in a mixed solvent of chlorobenzene and toluene in the ratio of 3:1 (by volume). The solution in both cases was filtered using a 0.2  $\mu\text{m}$  teflon filter. Films were prepared by spin-coating the solution on glass, silicon oxide on silicon and indium tin oxide (ITO) substrates. The solution viscosities and spin speeds were adjusted to produce films that are typically 1.0-1.2  $\mu\text{m}$  thick. The spin-coated samples were baked for about 12 hours at 50°C under vacuum to remove residual solvent.

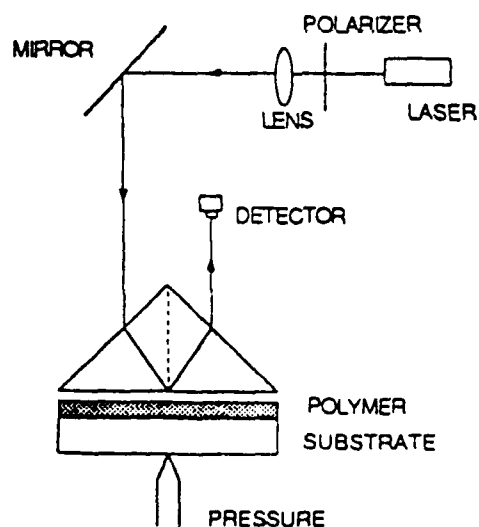


Figure 2. Schematic of waveguiding experiment using a prism coupler

## LINEAR OPTICAL PROPERTIES

Linear optical properties of PVCN were investigated using waveguiding technique. Thin film planar waveguides were fabricated on glass and  $\text{SiO}_2$  on silicon with the polymer as the guiding layer. A rutile prism was used to couple a light beam into the waveguide structure. The schematic of the waveguiding experiment using a prism coupler is shown in Figure 2. The reflected intensity from the prism was monitored as a function of the external angle of incidence. The coupling angles were obtained from the reflected intensity minima for both transverse electric (TE) and transverse magnetic (TM) polarizations. The dispersion

A.K.M. RAHMANN

1st page start Title here

equation of a planar waveguide structure for each polarization was solved to determine thickness and refractive index of PVCN film [11]. Two TE or TM Modes were observed for PVCN film on glass using a 633nm He-Ne source. Figures 3(a) and 3(b) show reflected intensity versus external angle of incidence for TE<sub>0</sub> and TE<sub>1</sub> modes. Figures 4(a) and 4(b) show reflected intensity versus external angle of incidence for TM<sub>0</sub> and TM<sub>1</sub> modes. The well resolved minima demonstrate the excellent optical quality of the film. The refractive index and thickness of PVCN before photocross-linking were found to be 1.60 and 1.16μm respectively using a 633nm He-Ne source.

1st page begin Abstract here

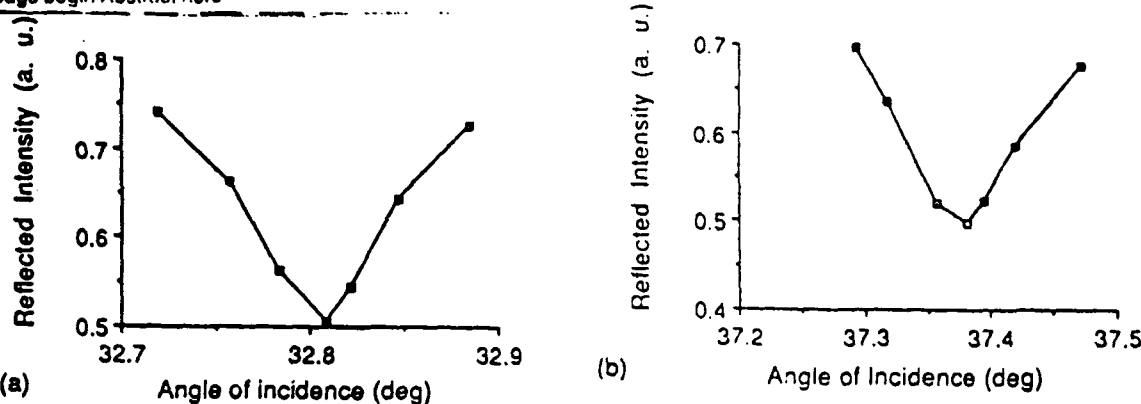


Figure 3. Reflected intensity vs angle of incidence for (a) TE<sub>0</sub> mode and (b) TE<sub>1</sub> mode

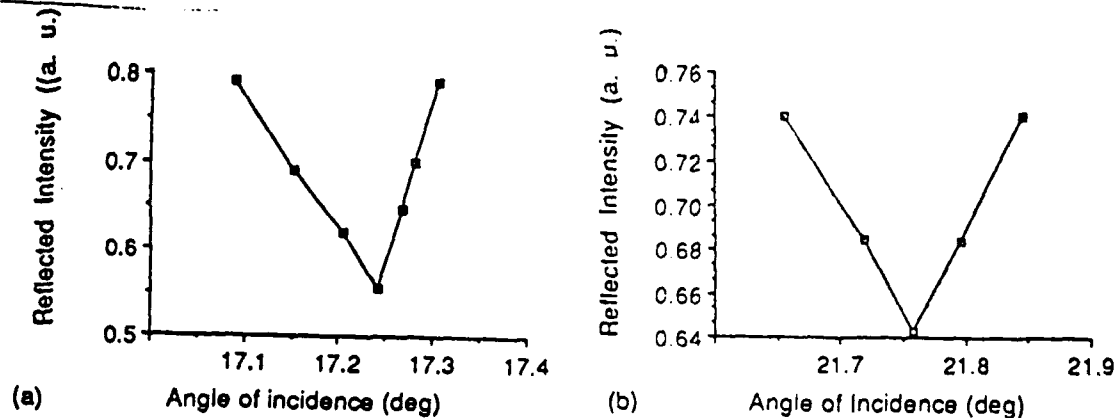


Figure 4. Reflected intensity vs angle of incidence for (a) TM<sub>0</sub> mode and (b) TM<sub>1</sub> mode

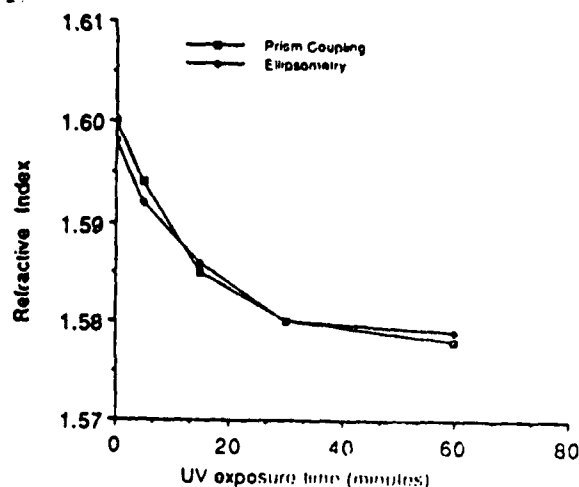


Figure 5. Refractive index vs UV exposure time ( $I = 2 \text{ mW/cm}^2$ ) for PVCN

A.K.M. RAHMAN

1st page start Title here

The cross-linking of PVCN was performed by irradiating UV light ( $\lambda = 254\text{nm}$ ) with an intensity of approximately  $2\text{mW/cm}^2$  on the film surface. Waveguiding technique was used to determine refractive indices of PVCN at  $\lambda = 633\text{nm}$  as a function of UV exposure time. The change in refractive index vs UV exposure time is plotted in Figure 5. The refractive index of PVCN decreases with photocross-linking. The decrease in the index of refraction is due to the loss of unsaturated double bonds which are converted into saturated four membered rings as a result of intermolecular cross-linking. No anisotropy was observed in PVCN before and after photocross-linking.

The refractive indices of PVCN before and after photocross-linking were also measured at  $633\text{ nm}$  using an ellipsometer and are plotted in Figure 5. The values of refractive indices were found to be in very good agreement with those obtained by the waveguiding technique.

Waveguide loss of PVCN was determined using an experimental setup shown in Figure 6. A fiber bundle was used as a probe to collect light scattered from the waveguide. The fiber was held at right angle to the waveguide and scanned along the length of the bright streak formed by the guided beam. The distance between the fiber end-face and the waveguide surface was kept constant during scanning and light passing through the fiber was monitored as a function of position. Loss was evaluated assuming [12]

$$I = I_0 \exp(-\alpha z)$$

where  $I$  is the intensity of scattered light at any point,  $z$  along the length of the waveguide,  $I_0$  is the intensity at  $z = 0$ , and  $\alpha$  is the attenuation coefficient. A plot of  $\ln(I)$  versus  $z$  for PVCN is shown in Figure 7. The waveguide loss for PVCN was found to be  $3\text{ dB/cm}$  at  $633\text{nm}$  wavelength. This loss is mostly due to scattering because the absorption loss for this polymer at  $633\text{nm}$  wavelength is negligible.

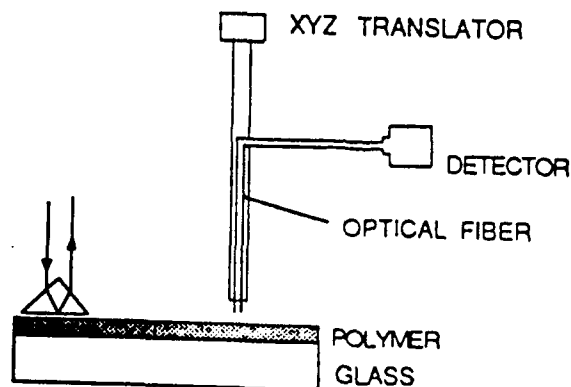


Figure 6. Schematic of waveguiding loss measurement system

#### ELECTRO-OPTIC MEASUREMENTS

The electro-optic coefficients of PVCN doped with 10% CNNB-R were measured using the reflection method of Teng and Man [13]. Schematic of experimental setup for this method is shown in Figure 8. A thin film ( $1\mu\text{m}$ ) of PVCN doped with CNNB-R was spun onto ITO coated glass. The polymer films were poled using both the corona poling and parallel electrode

A.K.M. RAHMAN

1st page start Title here

1st page start Authors here

1st page begin Abstract here

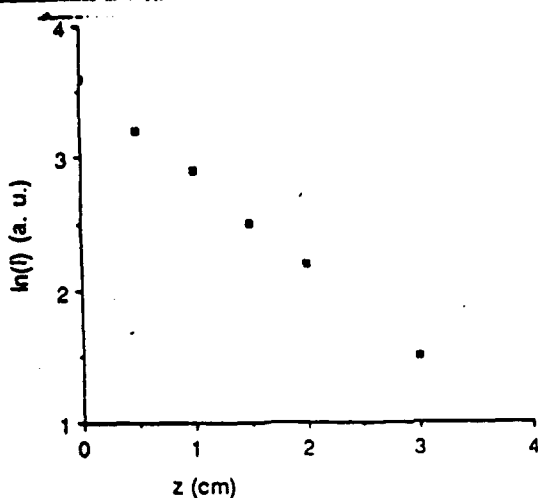
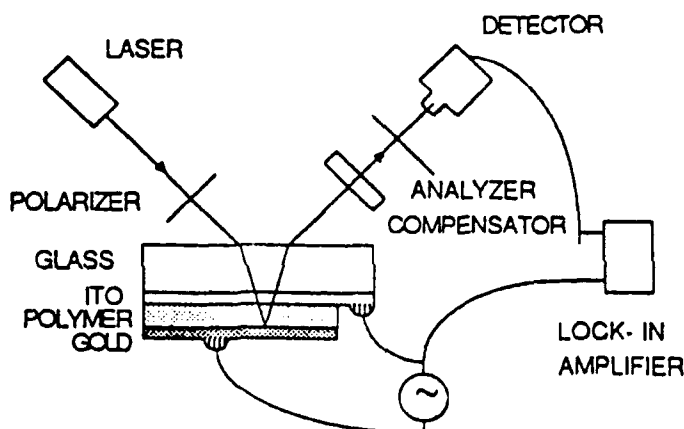
Figure 7. Plot of  $\ln(I)$  vs  $z$  for PVCN

Figure 8. Experimental arrangements to measure electro-optic coefficients

In the corona poling technique, the wire-to-plane electrode configuration was used. The poling temperature was  $70^{\circ}\text{C}$  which is less than the glass transition temperature  $T_g$  ( $T_g = 80^{\circ}\text{C}$ ). The polymer was poled for about 4 minutes and subsequently cross-linked for 10 minutes by UV irradiation without changing the poling field. The sample was then cooled down to room temperature under the poling field and with the UV lamp on. A thin layer (60nm) of polyvinyl alcohol (PVA) was deposited on top of the sample by spin coating PVA solution in water to fill the pinholes generated during corona poling. Gold film of 40 nm thickness was evaporated on top of the PVA layer. Gold and ITO served as top and bottom electrodes for modulating field for electro-optic measurements.

In the parallel electrode poling technique, gold electrode was first evaporated on top of the polymer layer. The sample was heated to  $70^{\circ}\text{C}$  and a voltage was applied between gold and ITO electrodes. The poling and cross-linking were then performed using the procedure described earlier.

The electro-optic coefficient is given [13] by

$$r_{33} = \left[ 3 \lambda I_m (n^2 \cdot \sin^2 \theta)^{3/2} \right] / \left[ 4 \pi v_m I_c (n^2 \cdot 2 \sin^2 \theta) n^2 \sin^2 \theta \right]$$

1st page start Authors here

## CONCLUSION

**Acknowledgement:** Funding for this research from ONR and a grant from the department of Air Force System Command are gratefully acknowledged.

## REFERENCES

1. F. Kajzar, J. Messler and C. Rosilio, J. of Appl. Phys., 60, 3040 (1986).
2. K. D. Singer, W. R. Holland, M. G. Kuzyk, and G. L. Wolk, SPIE, 1147, 233,(1989).
3. M. A. Mortazavi, A. Knoesen, S. T. Kowel, B. G. Higgins, and A. Dienes, J. Opt. Soc. Am., B6, 733 (1989).
4. J. Zyss, J. Molec. Electron., 1, 25 (1985).
5. K. D. Singer, J. E. Sohn, and S. J. Lalama, Appl. Phys. Lett., 49(5), 248 (1986).
6. R. D. Small, K. D. Singer, J. E. Sohn, M. G. Kuzyk, and S. J. Lalama, SPIE, 682, 160 (1987).
7. M. Eich, A. Sen, H. Looser, G. C. Bjorklund, J. D. Swalen, R. Tweig, and D. Y. Yoon, J. Appl. Phys. 66(6), 2559, (1989).
8. M. Eich, B. Reck, D. Y. Yoon, C. G. Wilson And G. C. Bjorkland, J. Appl. Phys. 66(7), 3241(1989).
9. B. K. Mandal, J. Kumar, J. C. Huang, and S. K. Tripathy, Makromol. Chem. Rapid. Commun. (in press).
10. B. K. Mandal, Y. M. Chen, R. J. Jeng, T. Takahashi, J. C. Huang, S. Tripathy, Eur. Polym. J., (in press).
11. R. Ulrich and R. Torge, Appl. Opt., 12, 2901 (1973).
12. L. M. Hayden, G. F. Sauter, F. R. Ore, P. L. Pasillas, J. M. Hoover, G. A. Lindsay, and R. A. Henry, J. Appl. Phys., 68, 456 (1990).
13. C. C. Teng and H. T. Man, Appl. Phys. Lett. 56(18), 1734, (1990).

И.Е.М. РАИАНН